The effects of residual polymerization solvent on the physical properties of poly(2-cyano-p-phenylene terephthalamide)

Dae Eon Jung,[1] Dong Jun Kim,[1] Youngho Eom,[1] Jaeyoung Lee,[2] Byoung Chul Kim[1]

[1]Department of Organic and Nano Engineering, Hanyang University, Seoul, Korea 04763
[2]Fundamental Technology R&D Group, Central Research Park, Kolon Industries, Inc., Gumi, Korea 446-797
Correspondence to: B. C. Kim (E-mail: bckim@hanyang.ac.kr)

ABSTRACT: Poly(2-cyano-p-phenylene terephthalamide) (CY-PPTA) was obtained by the polycondensation of terephthaloyl dichloride and 2-cyano-p-phenylene diamine in the mixture of N-methyl-2-pyrrolidone (NMP) and calcium chloride ($CaCl_2$). Washing the polymerized product with water and drying at the elevated temperature inevitably left a small amount of polymerization residues which could be eliminated only by additional washing with acetone. The thermogravimetric and ^{1}H-/^{13}C-NMR analyses revealed that the residues were largely composed of NMP which existed as a complex with the polymer. The complex was broken up between 200 and 300 °C and evolved 5 wt % of gaseous products, which had an adverse effect on the physical properties of as-spun CY-PPTA fibers obtained by dry jet-wet spinning. The heat treatment of the as-spun fibers including residual NMP exhibited some porous morphology on the fiber surface due to the evolved gases. However, the existence of the residual NMP had little effect on the intrinsic viscosity and liquid crystalline phase behavior of the polymer. Both rheological and optical properties exhibited the critical concentration at 3 wt % with the clear schlieren texture of nematic liquid crystalline phase. The inclusion of residual NMP decreased dynamic viscosity and yield stress. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43672.

INTRODUCTION

Para-Aramids, in which more than 85% of amide groups are attached to aromatic rings, give excellent mechanical and thermal properties because of high molecular rigidity and strong intermolecular interactions.[1–3] The interactions are derived from regular stacking of aromatic rings and hydrogen bonding of amide groups. These lead to high degree of molecular orientation and lyotropic liquid crystalline behavior. Thus, they are recommended to produce high tensile strength and modulus fiber through dry jet-wet spinning.[4–6] Such high performance enables the aramid fibers to be widely used in the production of bullet proof vests, protective apparels, aircraft body parts, and electromechanical cables.[7,8] Poly(2-cyano-p-phenylene terephthalamide) (CY-PPTA) is one of *para*-aramids where a nitrile group is attached to the phenylene diamine unit.[9,10] The randomly introduced nitrile groups would give an advantage of organo-solubility in the mixture of N-methyl-2-pyrrolidone (NMP) and calcium chloride ($CaCl_2$).

The use of NMP, one of highly polar organic solvents, was frequently reported to generate extraordinary strong complexes with polar groups of polymer chains. Ponzio *et al.*[11] investigated the influence of NMP residue on physical properties of polyaniline film where hydrogen bonding is formed between carbonyl groups of the solvent and hydrogens in the amine groups of polyaniline chains. The solvent molecules hindered the doping–dedoping process and could not be completely removed by water washing. The residual solvent complex was reported to be removed by heat treatment or protonation–deprotonation cycle process. The infrared spectra of polyaniline film exhibited that the carbonyl group peaks of NMP complex decreased via heating the film at 200 °C for 30 min. In the protonation–deprotonation cycle of polyaniline film, HCl solutions where the polyaniline film was soaked produced the delocalized radical cations resulting in partially positive charges on the amine nitrogen. This indicates that the complex is broken up by weakening hydrogen bonding. Nakauchi *et al.*[12] also reported that NMP and poly(m-phenylene isophthalamide) form crystalline complex and coexist in the crystal lattice.

The polymerized CY-PPTA solutions in NMP/$CaCl_2$ has a high potential of *in situ* dry jet-wet spinning, which may reduce contamination and production cost. However, we found out that a small amount of NMP remained as a complex in the *in situ* dry jet-wet spun CY-PPTA fibers after normal washing and drying
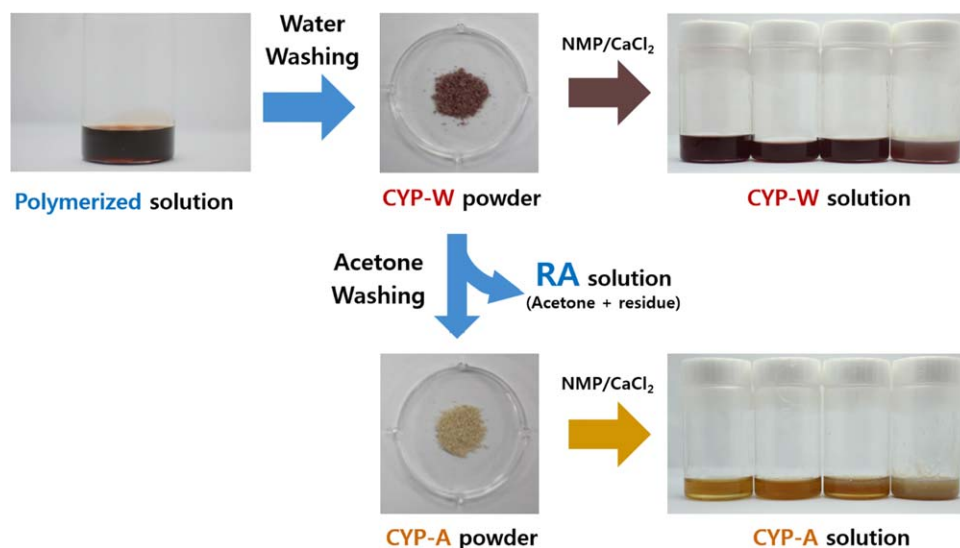
Figure 1. The overall washing procedure to prepare CYP-W, CYP-A, and RA solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

processes, which could be removed only by additional washing with acetone. Moreover, the complex was retained even in the solution state after the re-dissolution with NMP/CaCl$_2$ unlike the previous studies investigating the bulk. In this study, we identified and measured the residual polymerization solvent in the as-spun CY-PPTA fibers and examined their effects on the physical properties of CY-PPTA solutions and fibers.

EXPERIMENTAL

Materials

EP grade NMP (Daejung Chemicals Co., Korea) and HPLC grade water (Daejung Chemicals Co., Korea) were used without further purification. CaCl$_2$ (JunseiChemical Co., Japan) was vacuum dried 24 h prior to use. Terephthaloyl chloride (TPC) and calcium oxide (CaO) were purchased from Aldrich Co.

(USA). TPC was purified by vacuum distillation. CY-PPTA solution was prepared by the polycondensation of terephthaloyl dichloride (TPC) and 2-cyano-p-phenylene diamine (CYPPD). Firstly, CaCl$_2$ was dissolved in NMP, followed by the addition of CYPPD in nitrogen purging. After CYPPD was completely dissolved, TPC was added with vigorous stirring. Then, CaO was added to neutralize the polymerized solution after the completion of polymerization. Then 15 wt % CY-PPTA solution
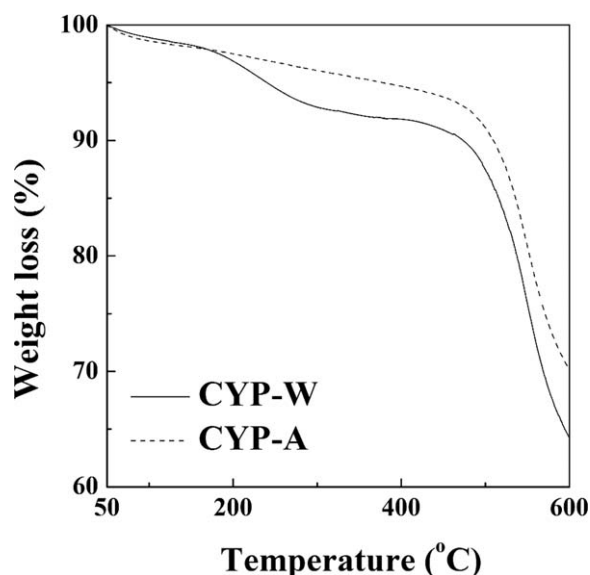

Figure 2. The TGA thermograms of CYP-W and CYP-A in N$_2$ atmosphere at the heating rate of 10 °C/min.
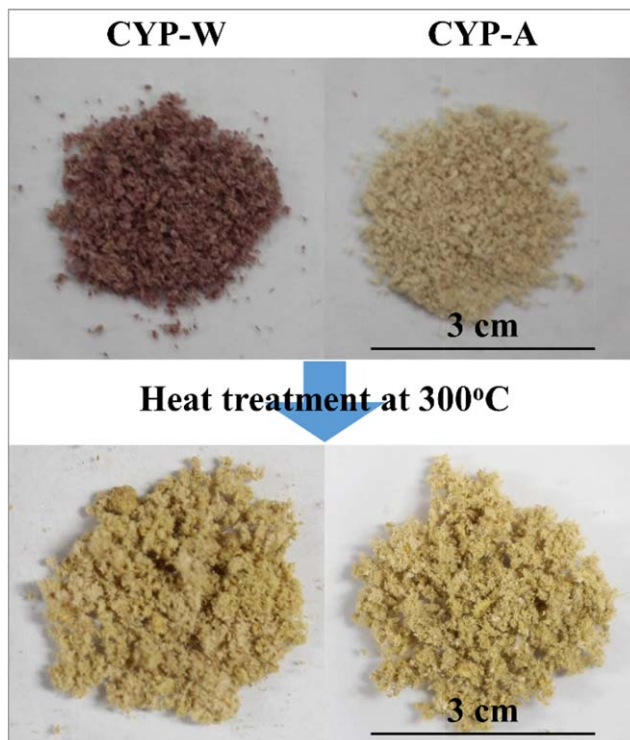

Figure 3. Photographs of fresh and heat-treated at 300 °C CY-PPTA powders. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
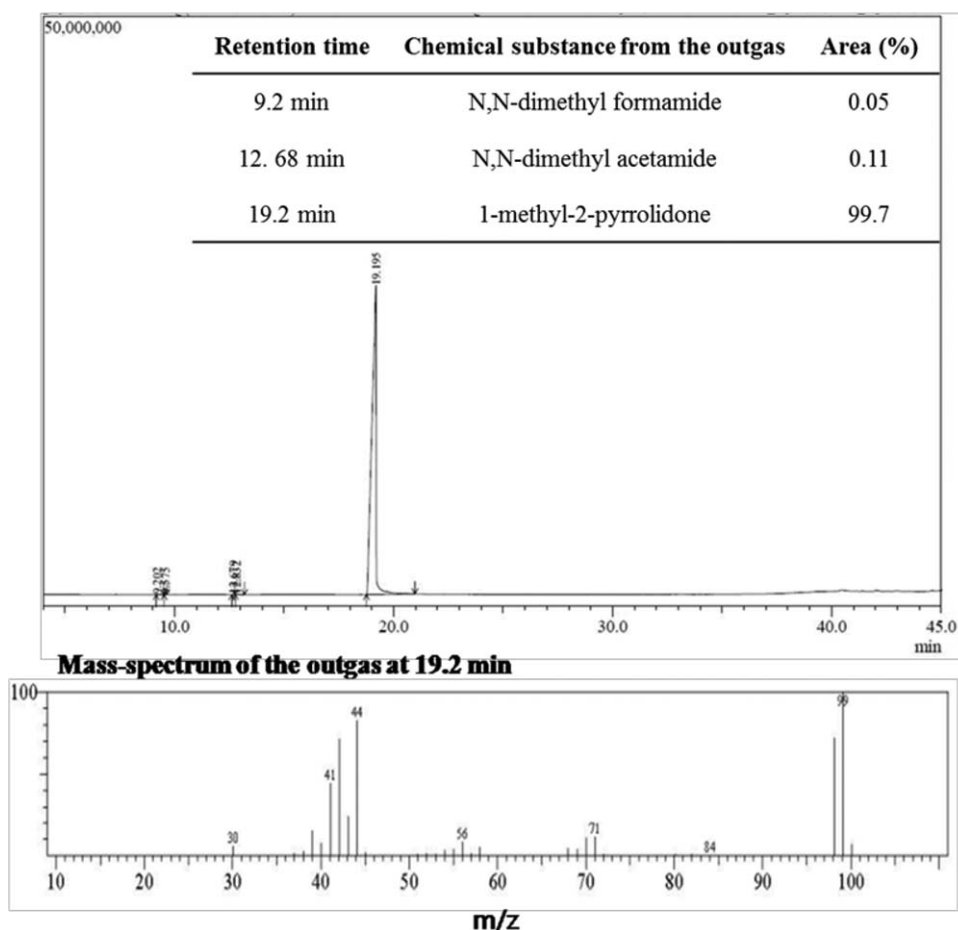
Figure 4. Tds-GC-MS plot for the outgas analysis at 300 °C.

with 8.2 wt % of CaCl$_2$ and 76.8 wt % of NMP was obtained. CY-PPTA including residual NMP (CYP-W) was obtained by spilling the polymerized solution into the water bath where water was mechanically stirred, then the mixture was grinded in the home mixer. CYP-W powder was vacuum dried for 24 h to completely remove water. CY-PPTA without residual NMP (CYP-A) was prepared by extracting the NMP residue from CYP-W with acetone for 12 h, followed by 24 h vacuum drying to completely remove acetone. The acetone including NMP by washing CYP-W powder was named as RA solution. The overall washing procedure is shown in Figure 1. CYP-W and CYP-A powders were re-dissolved in the mixture of NMP and CaCl$_2$ where the salt and polymer contents were 5 and 12 wt %, respectively. The solutions were mechanically stirred 48 h at 60 °C. The 0.01–0.9 g/dL and 2–10 wt % solutions of CYP-W and CYP-A were prepared by adding additional solvent to 15 wt % of CYP-W and CYP-A solutions, respectively. CY-PPTA fibers were prepared by direct dry jet-wet spinning of *in situ* polymerized CY-PPTA solution dope composed of 15 wt % of CY-PPTA, 8.2 wt % of calcium chloride (CaCl$_2$), and 76.8 wt % of NMP.

Measurement of Physical Properties
RA solution was dried at 60 °C for 24 h to remove acetone and then measured by ^{1}H- and ^{13}C-NMR. The spectra were obtained on a JEOL Oxford 600 spectrometer operating at 600

MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent. The thermal properties of CYP-W and CYP-A powders were examined by thermo-gravimetric analysis (TGA; Pyris 1, Perkin–Elmer, USA) at the scanning rate of 10 °C/min under nitrogen atmosphere. The thermodesorption analysis of the CYP-W powder was carried out with Perkin–Elmer Turbo Matrix Automated Thermal Desorber 350 at 300 °C for 30 min. The generated outgas from the thermal desorber was analyzed by gas-chromatography and mass-spectrometry (QP-2010 Series GC/MSD system, SHIMADZU, Japan).

The reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) of CY-PPTA solutions were measured by Ubbelohde viscometer (Schott Co., Germany) and calculated by eqs. (1) and (2), respectively,

$$\eta_{red} = \frac{t - t_o}{t_o c} \tag{1}$$

$$\eta_{inh} = \frac{\ln (t/t_o)}{c} \tag{2}$$

in which, c is concentration and t_o and t are the efflux time of the solvent and the polymer solution, respectively. The rheological properties of CY-PPTA solutions were measured by AR-550 (TA instruments, USA). Parallel-plate geometry with a diameter of 40 mm and the gap of 800 μm was adopted. The strain level
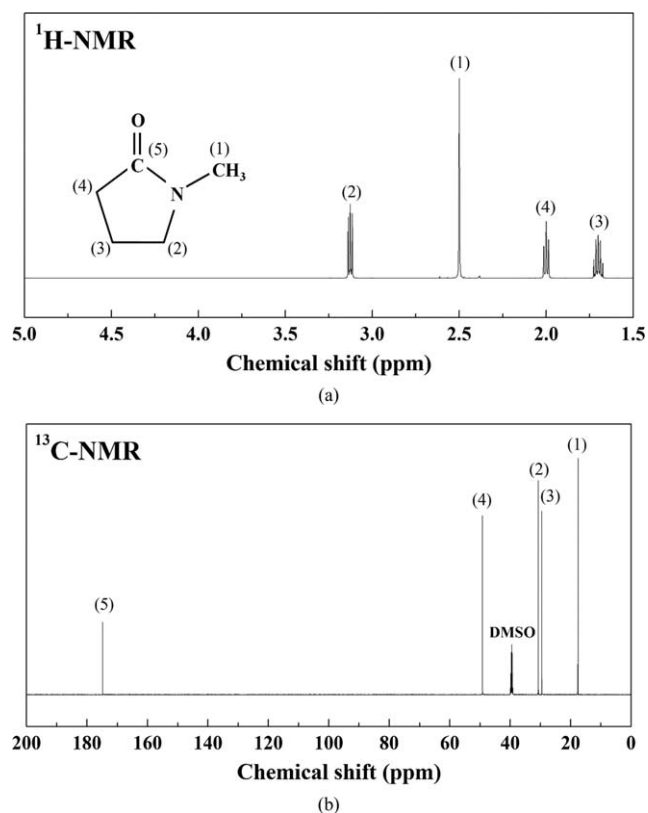
Figure 5. (a) ^{1}H- and (b) ^{13}C-NMR spectra of the residual solution (RA).

for the solution was 5%. The samples were placed in the plates for 20 min to fully relax the residual stresses of the solutions. To prevent the solvent evaporation, heavy mineral oil (Sigma Aldrich Co., USA) was covered on the edge of the plates. Dynamic frequency sweep experiment was conducted over the frequency range of 0.05–200 rad/s. The liquid crystalline textures of CYP-W and CYP-A solutions were observed by a polarized optical microscope (Olympus BX51, Japan) with CCD camera (Olympus DP70, Japan). The tensile test was conducted with a universal testing machine (Instron 4465 model, USA) at 30°C. The crosshead speed was 10 mm/min. Measurement was repeated six times for each sample and the average values were taken as data. The field emission scanning electron microscopy (FE-SEM) images of the fractured surface of the as-spun and heat-treated fibers were obtained using a JEOL JSM-6340F (Japan) to evaluate the morphology.

RESULTS AND DISCUSSION

TGA thermograms of CYP-W and CYP-A powders are shown in Figure 2. Both powders show a rapid decrease of weight in the vicinity of 480°C due to the thermal decomposition.[13] However, CYP-W powder gives an additional sudden reduction of weight, 5 wt %, over the temperature range of 200–300°C, suggesting the evaporation of some volatile components. In addition, the dark-red CYP-W powder turned to a yellow color after heat treatment for 30 min at 300°C, almost the same color as the CYP-A powder as shown in Figure 3. This suggests that both CYP-W and CYP-A may have similar physical state after the elimination of the volatile components. The chemical composition and structure of the loss material are traced by using tds-
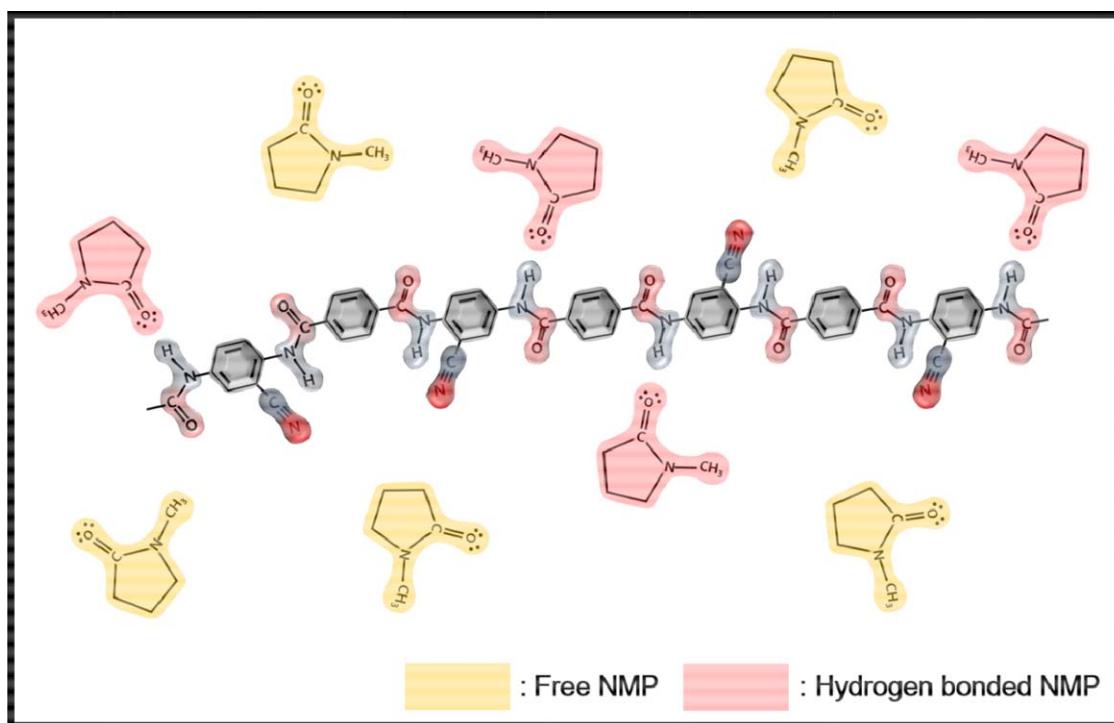
Scheme 1. Schematic representation of physical states of free and hydrogen bonded NMP molecules in CY-PPTA solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
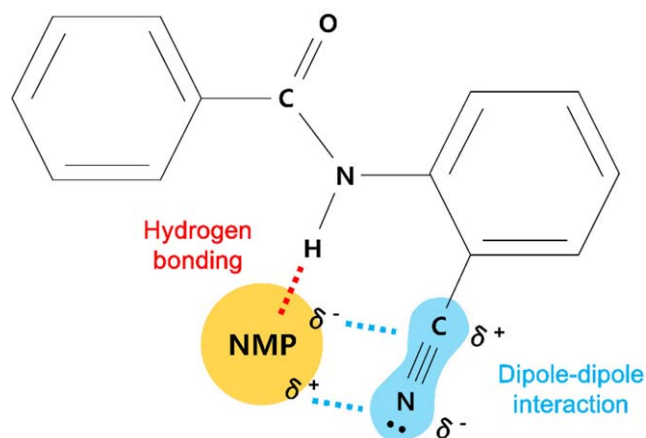
Scheme 2. Schematic representation of NMP molecules generating dipole–dipole interaction with the cyano group and hydrogen bonding with the amide group of CY-PPTA chain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

GC-MS. Figure 4 shows the tds-GC-MS spectrum of CYP-W powder at 300 °C. A strong peak is observed at the retention time of 19.2 min, at which 99.7 wt % of the gas was captured. The mass-spectrum of the captured gas informs that the outgas is mostly composed of NMP. This is further supported by ^{1}H-/^{13}C-NMR spectra of RA solution as shown in Figure 5. The peaks of the residues extracted from the CYP-W powder by additional acetone washing correspond to NMP.

It is worth noting that NMP molecules, whose boiling point is 200 °C, are retained up to 300 °C in the TGA thermogram of the CYP-W powder. This indicates that the residual NMP molecules are more strongly captured by CY-PPTA chains than when they are in bulk state.[14,15] Highly polar organic solvents are known to form extraordinary strong bonds or complexes with polar groups of polymer chains, which are often called the "bound organic solvent."[16–18] NMP, one of the highly polar organic solvents, is a strong hydrogen bonding acceptor. Thus, NMP molecules form hydrogen bonding with amide groups of CY-PPTA chains in the solution as shown in Scheme 1. Then NMP molecules can be divided into two categories according to their physical state in the solution. One is free NMP molecules which generate dipolar interactions each other and the other is bound NMP molecules which form hydrogen bonding with CY-PPTA chains. Free NMP molecules would be easily washed with

Table I. Overall and Individual Solubility Parameters of Acetone, NMP, and PPTA at 25 °C

	Solubility parameter (MPa$^{1/2}$)			
	δ	δ_d	δ_p	δ_h
Acetone	20.1	15.5	10.4	7.0
NMP	22.9	18.0	12.3	7.2
PPTA	23.0	18.0	11.9	7.9

The solubility parameter is given by the sum of the dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) contributions; $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$.
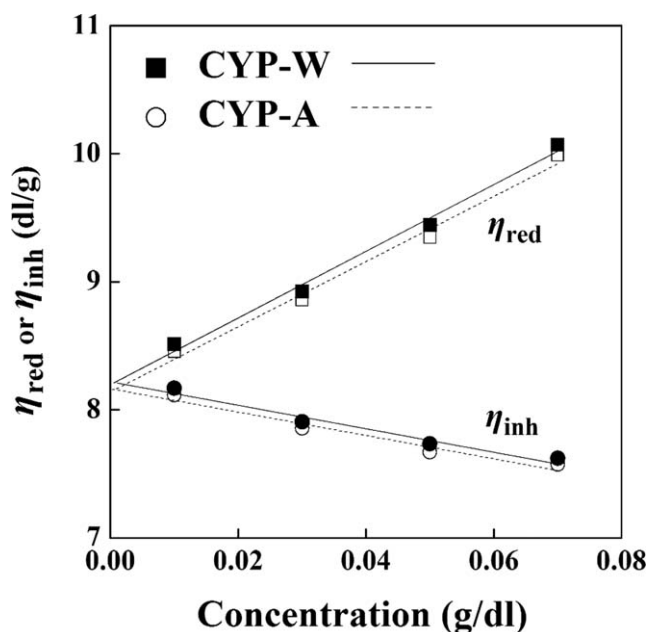

Figure 6. Plots of η_{red} and η_{inh} against concentration for CY-PPTA solutions at 30 °C.

water but the bound NMP molecules could remain in the CYP-W powder.

The introduced cyano groups to both sides of CY-PPTA chain would give rise to the organo-solubility of CY-PPTA by making effective hydrogen bonding more difficult. At the same time, however, pendant cyano groups would form a complex. Once NMP molecule is confined in the powder hydrogen bonded with the amide group, adjacent polar cyano group strongly polarizes NMP molecule through dipole–dipole interactions as illustrated in Scheme 2. This means two kinds of interactions,
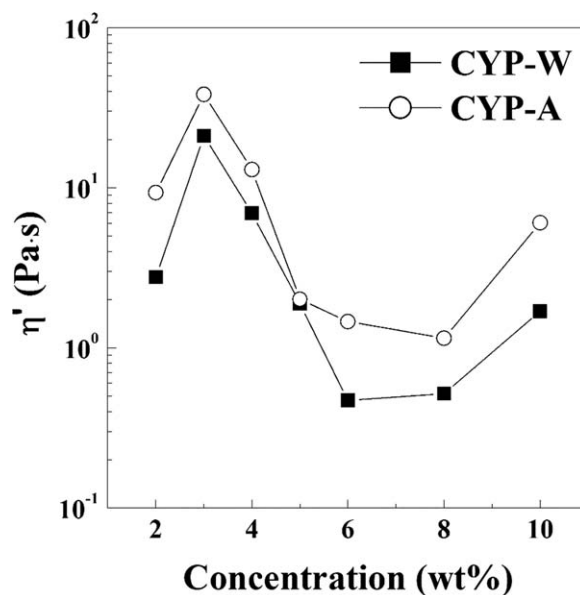

Figure 7. The critical concentration curves of CY-PPTA solutions at 0.5 rad/s. The solvent for the solutions is composed of NMP containing 5 wt % of CaCl$_2$.
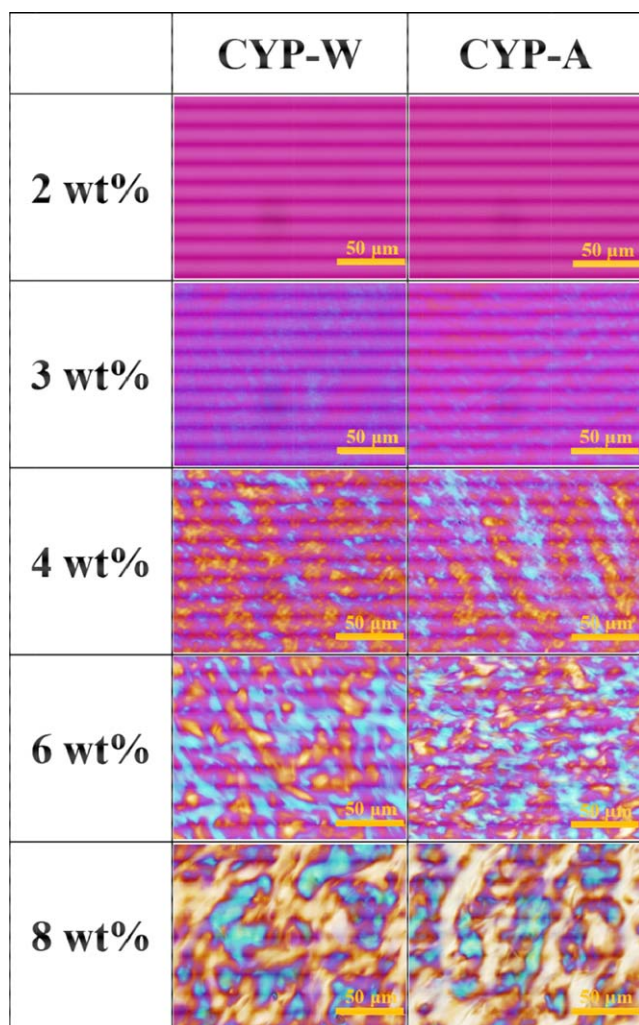
Figure 8. Polarized optical micrographs (100×) of CY-PPTA solutions. The units in the left column stand for the concentration of CY-PPTA solutions in NMP containing 5 wt % of CaCl₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen bonding and dipole–dipole interaction, should be provided to eliminate this complex. That is, it is hard to remove it through the simple re-dissolution process with NMP, but additional washing the CYP-W powder with acetone can extract the residual NMP. Table I lists the solubility parameters of NMP, acetone, and poly(p-phenylene terephthalamide) (PPTA). The overall solubility parameter (δ) is calculated by the sum of the dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) contributions ($\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$), which represents the strength of physical bonding of a material.[19] As expected, all have similar values of δ_h term. Then, the effective elimination of the residual NMP molecules from the CYP-W powder is ascribable to close to δ_h term between acetone and NMP.

The reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) of CY-PPTA solutions are plotted against concentration in Figure 6. Extrapolating the η_{red} and η_{inh} curves to zero concentration gives intrinsic viscosity [(η)] which is a measure of coil dimen-
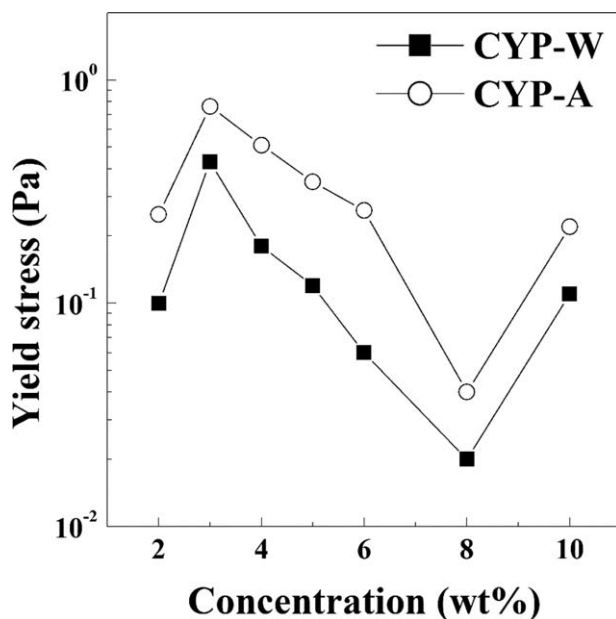

Figure 9. Plots of yield stress (G''_y) against concentration of CY-PPTA solutions. The solvent for the solutions is composed of NMP containing 5 wt % of CaCl₂.

sion of a polymer in a solvent.[20,21] In the figure, CYP-W and CYP-A solutions give almost the same value of [η]. This means that bound NMP molecules hardly change the hydrodynamic volume of CY-PPTA chains in the solution. In other words, the existence of the residual NMP complex has little influence on the conformation of CY-PPTA chains.

Figure 7 shows the critical concentration (C^*) curve of CY-PPTA solutions. Both solutions exhibit comparable lyotropic liquid crystalline behavior with a clear C^* at 3 wt %. Polarized
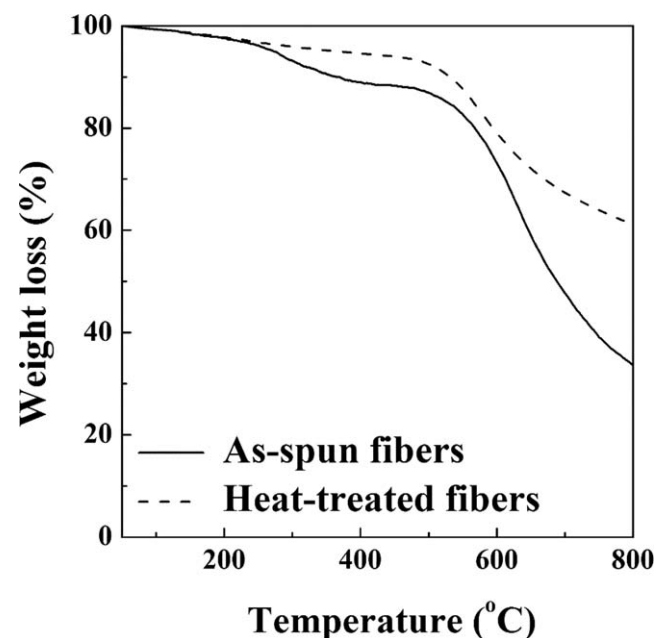

Figure 10. The TGA thermograms of as-spun and heat-treated fibers in N₂ atmosphere at the heating rate of 10 °C/min.
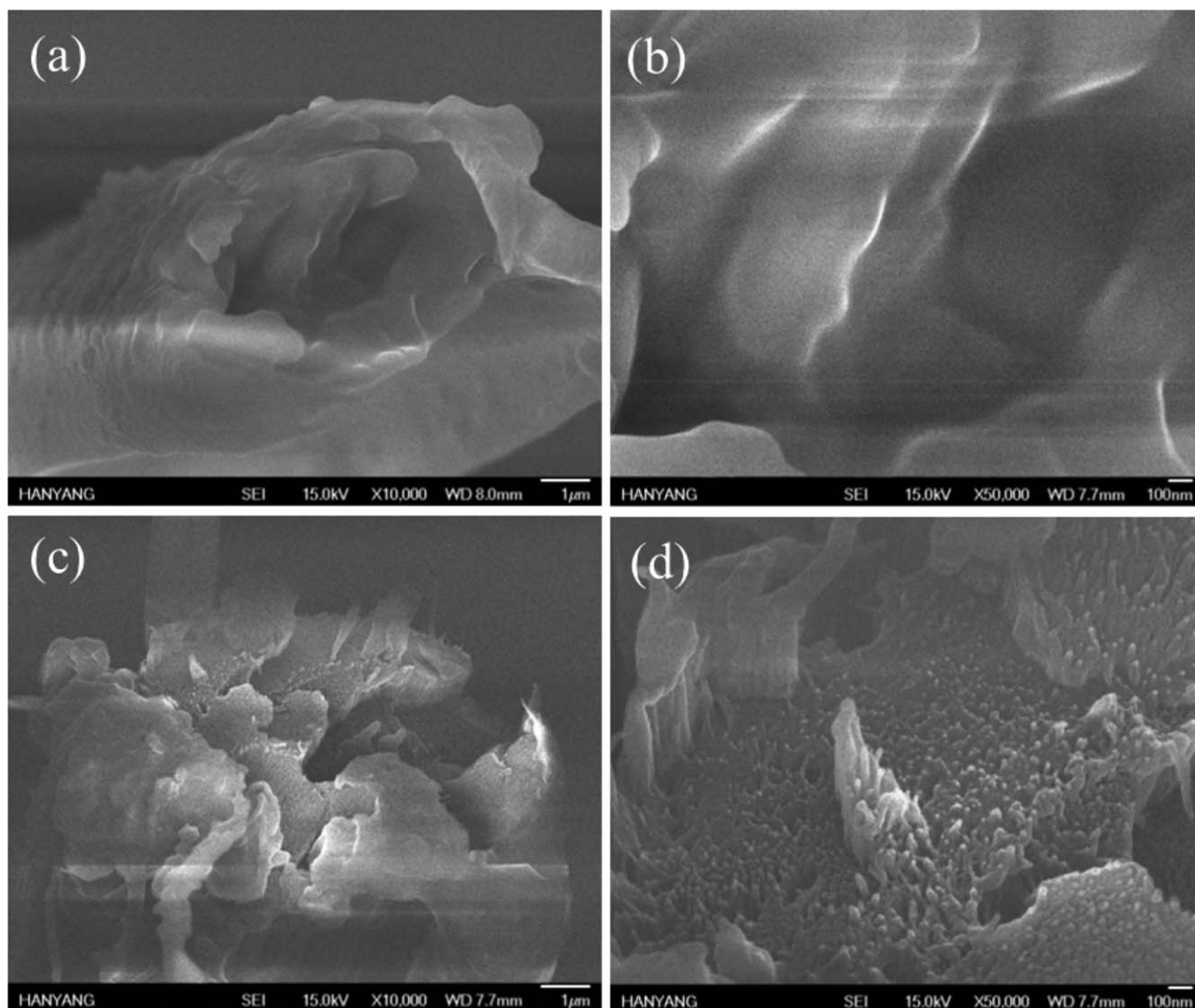
Figure 11. FE-SEM images of the fractured surface of CY-PPTA fibers; (a) and (b) for as-spun fibers, and (c) and (d) for heat-treated fibers.

optical micrographs of CY-PPTA solutions visually verify the phase behavior. In Figure 8, 2 wt % solutions do not develop any texture but the schlieren texture of nematic liquid crystalline phase starts to be observed at 3 wt % in both solutions. These results suggest that the C^* is little affected by the presence of the NMP complex. The C^* is known to be determined by the aspect ratio of a rod-like polymer.[22] The conformation of linkage groups in the rod-like polymer is a key factor for the aspect ratio of the polymer. Then, the comparable phase behavior is ascribed to the similar conformation of CY-PPTA chains in both solutions, which well coincides with the $[\eta]$ result.

In Figure 7, however, the dynamic shear viscosity (η') of CYP-A solutions is much higher than that of CYP-W solutions. In polar polymers, the strong intermolecular interactions of polar groups between polymer chains bring about the increase of apparent viscosity. Thus, the lower viscosity of CYP-W solutions suggests that bound NMP complex may hinder hydrogen bonding between amide groups of CY-PPTA chains. As a result, CYP-A solutions would generate more heterogeneous internal structures through the strong intermolecular interactions. The heterogeneity of a polymer solution can be further ascertained by the presence of yield stress, the threshold energy to break pseudo-structures. It can be determined by eq. (3),

$$G''1/2 = G_y''^{1/2} + K'\omega^{1/2} \tag{3}$$

in which, G'' is loss modulus, G_y'' is yield stress, K' is constant, and ω is frequency.[23–25] The yield stress obtained from the intercept of G''-axis at $\omega = 0$ is shown in Figure 9. On the whole, CYP-A solutions give greater values of yield stress than CYP-W solutions. Consequently, the elimination of the residual NMP molecules seems to be more efficient for intermolecular interactions between CY-PPTA chains.

The direct dry jet-wet spinning of the *in situ* polymerized CY-PPTA solution dope undoubtedly leaves some residual NMP in the as-spun fibers. TGA thermograms of the as-spun fibers prepared by normal water washing and fibers prepared by heat treatment of the as-spun fibers for 30 min at 300 °C are shown in Figure 10. The as-spun fibers show 5 wt % weight reduction
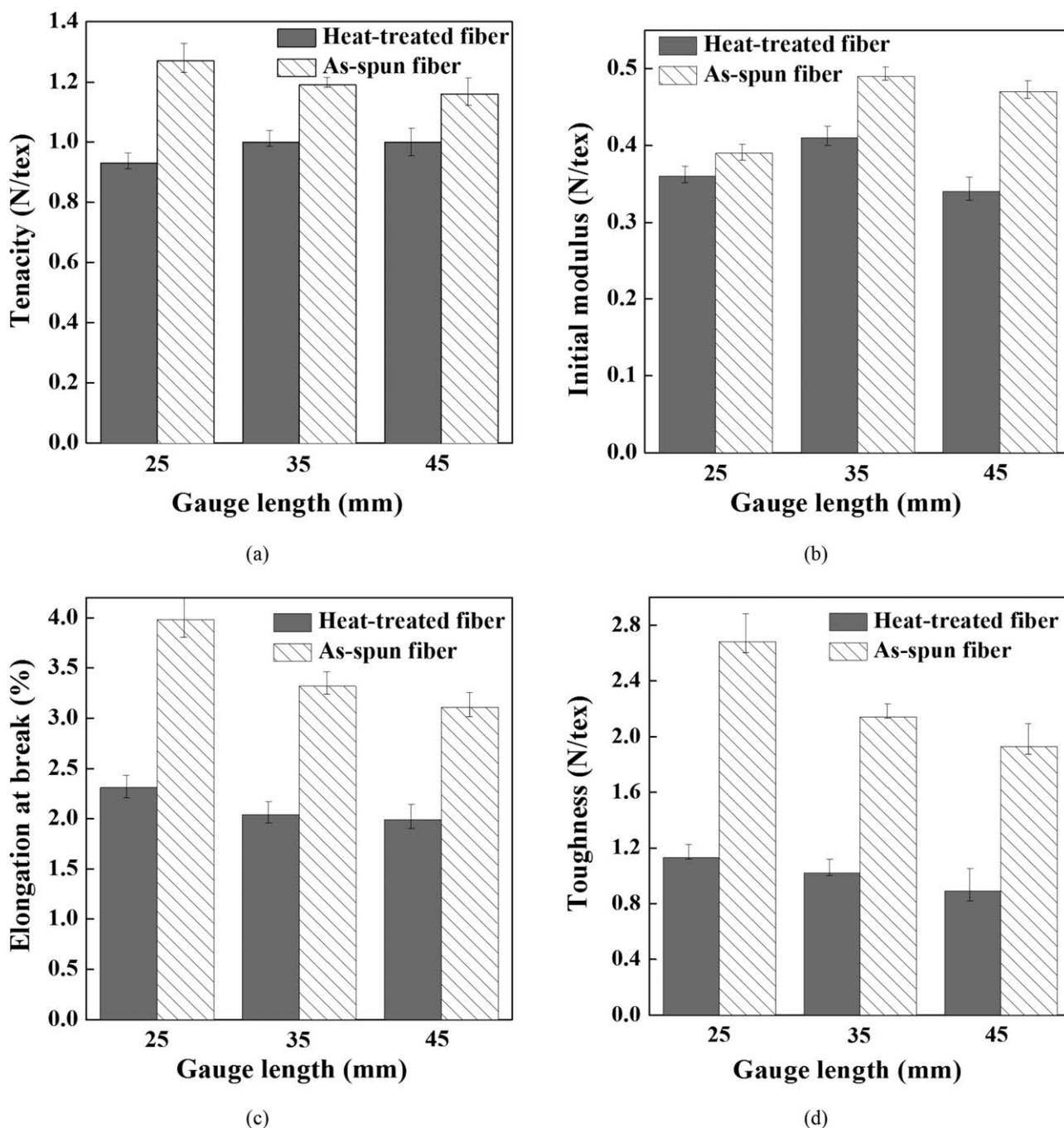
Figure 12. Tensile properties of heat-treated and as-spun fibers of CY-PPTA: (a) tenacity, (b) initial modulus, (c) elongation at break, and (d) toughness.

over the range of 210–350 °C similar with the CYP-W powder, suggesting that the residual NMP in the fibers may evaporate during the heat treatment. This can be morphologically verified by SEM images of the fractured surface of the heat-treated fibers in Figure 11. The evaporation of the residual NMP leaves porous and rough surface in the heat-treated fibers while the as-spun fibers show a smooth surface. Figure 12 shows the tensile properties of the as-spun and heat-treated fibers. As expected, the heat-treated fibers shows large drop of tensile properties compared to the as-spun fibers. Voids generated by the solvent evaporation decreases the compactness of the fibers,

reducing the initial modulus of the fibers. Further, such holes play a role of defect in the heat-treated fibers, bringing about the earlier fracture of the fibers with lower elongation at break and tenacity. Consequently, the toughness of the heat-treated fibers is much lower than that of the as-spun fibers.

CONCLUSIONS

The polymerized CY-PPTA solution left some residual NMP after normal water washing and drying processes due to strong hydrogen bonding between NMP and amide groups of CY-

PPTA. The NMP complex could be removed only by additional acetone washing. It gave rise to some porous morphology in the fiber which deteriorated the tensile properties of the fiber. The NMP complex affected the rheological properties of CY-PPTA spinning dope but had little influence on the conformation and liquid crystalline behavior of CY-PPTA.

ACKNOWLEDGMENTS

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